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Insights into the relationship between inherent materials properties of PZT and photochemistry for the development of nanostructured silver.

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Abstract

Recently there has been great interest in using patterned ferroelectric materials for the photochemical growth of metal nanostructures. Variations in surface and sub-surface structure influence the photochemical processes. Here we show that crystallography, and hence remnant polarization, of the ferroelectric affects photo-deposition. The ratio of metal growth on c^- and c^+ domains varies from 1:2 for [100] to 1:100 for [111]. This is shown to be dependent on the variations in the band structure.

Key words: PZT, photochemistry, nanometal

The desire to produce highly defined and well controlled metal nanostructures has been an area of research that has been gaining interest. Such metal nanostructures have a wide variety of applications that range from interconnects for nanoelectronic devices[1] and sensors for biological systems[2]. One technique that has been increasingly investigated over the past 5 years is ferroelectric lithography, which was first reported by Giocondi and Rohrer[3] in 2001 and then further investigated by Kalinin *et al*[4] where the term ferroelectric lithography was first used. Since that time further work has shown that surface features on the ferroelectric[5], energy of irradiation[6] and defect density[7] can all affect the density and morphology of metal nanoparticles produced by photoexcitation of the ferroelectric. Where it is possible to reproduce with good fidelity a nanostructure, there exists an opportunity to generate a nanolithographic technique. Where this is not possible there may exist a method to produce interesting nanostructures that can subsequently be removed and be useful elsewhere. Previously it has been shown that ferroelectric materials can be made with surface features as fine as 7nm with good structural control[8,9.]

When the bulk of a ferroelectric is broken by an interface such as a surface or grain boundary a depolarization field forms. Two possible screening processes can occur to produce an energetically stable state; one internal, the other external to the material. If we thinking of lead based ferroelectrics such as lead zirconate titanate (PZT) as wide bandgap semiconductors[10,11] rather than pure insulators then we are able to describe the behaviour of the material in terms of standard semi-conductor theory[4]. The work by Kalinin *et al*[4] and Giocondi *et al*[3] show that band bending due to the ferroelectric nature of the material has a major impact on the photochemical reactions that take place on the surface.. There is, however, one factor that must be considered; domain dependant polarization effects. Ferroelectric materials such as PZT have a macroscopic polarization that induces the accumulation or depletion of charges at the surfaces. In positive domains, a positive polarization charge is present at the surface of the material. Internal screening takes the form of a space-charge region forming due to

band bending when in close proximity to the interface. The polarization of the surface of the ferroelectric is dependant on the orientation of the ferroelectric domain due to the dipole developed in the distorted crystal lattice. Previous work has commented that the space charge region does not form complete screening of the internal dipole[12]. Therefore an external mechanism exists, which consists of the adsorption of foreign charged molecules at the surface. This is described by classic Derjaguin, Landau, Verwey, Overbeek (DLVO) theory and is the Stern layer associated with charged surfaces. In both types of domain, the polarization field is cancelled at equilibrium by the screening mechanisms.

When the ferroelectric is exposed to high energy ultraviolet light, electron-hole pairs formed near or within the space-charge region are driven apart by the internal electric field.[13] Mobile electrons are then forced to migrate to the surface of positive domains[14] and towards the bulk in negative domains. If a positive domain is immersed in a metal salt solution such as $AgNO_3$ and exposed to ultraviolet light, the accumulated electrons below the surface can react with the Ag^+ cations in solution. These electrons tunnel across the barrier and reduce the silver cation to form metal atoms that are adsorbed on the ferroelectric surface. Giocondi *et al*[3] pointed out that the adsorption of the Ag onto the surface cannot be ion polarization dependant as the Ag^+ ions and the surface of the ferroelectric c^+ domain are both positive. This means that the ion should be repelled if the process was polarity driven. The successful formation of the silver clusters supports the theories of Zhu and Kalinin. Further work has shown that the density of states of the ferroelectric material and the energy of irradiation can impact on the photochemical deposition process[6]. By irradiating a sample of PZT with a high dose of high energy photons a different pattern of photo-deposited silver metal was seen to that of a lower energy source[6]. The differences in the deposition of the silver were explained in terms of the density of states of the PZT and changes in the band bending.

PZT films, with the zirconium/titanium ratio of 30/70, were made using sol-gel (maximum processing temperature of 530ºC). The sol was then spin coated onto a prepared substrate, which in

our case was 100nm of Pt sputtered onto either [100] MgO or [111] Silicon[9]. The sample was $1cm^2$. The PZT films exhibited good [111] orientation if grown on Si or good [100] orientation if grown on MgO, orientation as determined by X-ray diffraction (XRD) and consisted of discrete 70-100nm grains with a random domain orientation, as determined by Piezo Force Microscopy (PFM). The films are fully dense, as determined by TEM examination, and show very little texturing in the x/y plane. The average grain size is 100nm for [111] samples and 200nm for [100] samples.

PFM was performed using a modified DI 3000 Atomic Force Microscope (AFM) system, the base electrode of the sample was connected to the ground of a signal generator and the conductive cantilever connected to the signal output. The signal generator was set to 18 kHz at $3V_{pk-pk}$. In order to avoid running the tip bias signals though the AFM a cantilever holder was modified to accept a direct connection to the tip via a trailing wire. The output of the AFM was run though an EG+G 7260 lock-in amplifier which was then passed back to the AFM for processing. The cantilevers used were platinum iridium coated and had a spring constant of k=1-5 N/m. Poling of the samples was undertaken by connecting the sample base electrode and conductive cantilever to a DC power supply set at 10V. For positive domains the tip was connected to the negative and the base to the positive power supply terminals and for negative domains they were switched. The samples were imaged using a Philips XL30 SFEG scanning electron microscope (SEM) in high resolution mode and the beam energy was set at 20keV and the aperture to 3. The samples were fixed to a holder by carbon tape and electrodag used to ground the sample base electrode to the holder.

Fresh solutions of 0.01M $AgNO_3$ were prepared by dissolving the required mass of silver nitrate (Aldrich 99.99%) in distilled water. The solution was used as is and the pH was not adjusted. A single drop of approximately 25μl of solution was placed onto the PZT surface which was then placed into a 'black out' box containing the lamp for irradiation. Inside the box the sample was placed onto a peltier device that kept the substrate temperature to that of room temperature. A 'Honle H 400W' lamp sits

directly above the sample and the radiation intensity at the sample is approximately 21mW. The 'black out' box is fitted with fans to reduce the temperature in the box which never exceeds room temperature plus 10ºC. Irradiation periods of 20 minutes were used during the investigation within experimental conditions there was no noticeable loss of volume for the solution.

In our recent work[6] we have compared the deposition of silver on a domain patterned thin film PZT (70nm) that was grown on a Pt back electrode and was either [111] or [100] orientated. It has been known for some time that PZT grown in various crystallographic orientations has a different remnant polarisation. This values associated with PZT are consistently that P_r for [100] is 60% of that for [111] orientated material[15]. These experimentally derived figures fit well with the mathematically determined figures[16]. The present study is focused on the impact of the differences of remnant polarization on the band structure at the surface of the ferroelectric. Experimentally the differences in the band structure are shown through a variation in the rate of deposition of Ag^0 where reduction from Ag^+ had occurred. In Figure 1 we show a typical SEM micrograph of the deposition of Ag on the surface of patterned PZT. Figure 1 (a) shows a 70nm PZT film with the crystallographic orientation [100] that has been irradiated under silver nitrate for 20 minutes. The boundary between the c^- and c^+ domain is clearly defined in the image. Figure 1 (b) shows a 70nm PZT film with the crystallographic orientation [111], once again irradiated in silver nitrate for 20 minutes. There are some striking differences in the deposition of silver on the PZT surface. In the case of the [100] sample there is good decoration on both the c^+ and c^- domains. However, on the surface of the PZT [111] there is no visible coverage on the c^- surface whereas the c^+ surface is covered in silver. In all cases the presence (or absence) of silver was determined using energy dispersive x-ray analysis (EDX). We have shown in previous work that the growth rate of silver nanoparticles is strongly dependent on the surface features of the ferroelectric[5]. In this case the probability of an electron tunnelling and reacting with a silver cation is the likely rate determining step. The lack of a barrier on the c^+ domain means that the rate of silver growth is similar for both surfaces studied. However, the variation in the band structure does

mean that the silver grows to an average particle size of 118nm on c^+ [100] and 93nm, on c^+ [111]. There is a larger difference in the size of the silver nanoparticles on the c^- ranging from no deposition ([111]) to a deposition of particles with an average diameter of 56nm ([100]). The variation in deposition rate on the c^- domain is representative of the lower probability of the electron crossing the barrier and reacting with a silver cation.

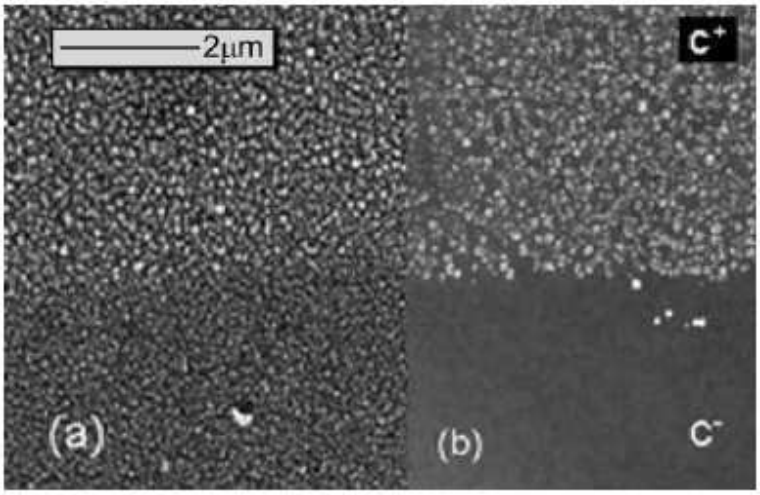

Fig. 1 SEM micrographs of silver decoration on [100] PZT (a) and [111] PZT (b) after 20 min of irradiation with a Honle H lamp. Silver deposition is present in the c^+ domain for both crystal orientations. However, on the c^- domains silver is only deposited onto the [100] sample.

The differences in deposition on the PZT surface can be explained in terms of the modification of space charge layer (SPL) due to the variation in the remnant polarisation of the sample. If it is assumed that there is incomplete internal charge screening, described as type 2 screening by Kalinin and Bonnell[17] and that charge screening is completed using external charges then the shape of the SPL varies due to the change in remnant polarization.

In the surface of a ferroelectric, there are two main sources of charge: the polarization charge (Q_P) and the charge due to surface states (Q_T). The effective charge on the surface Q_S is the sum of these two contributions with their respective signs, $Q_S=Q_P+Q_T$. The presence of this surface charge induces a space-charge region under the surface, with an associated band bending. The direction of bending

depends on the sign of the surface charge Q_S. Another compensation mechanism for this superficial charge is the adsorption of charged molecules from the surroundings.

The sign of the polarization charge depends on the polarity of the domain, being positive for c^+ domains and negative in c^- domains. Oxygen vacancies are mostly responsible for the surface states, as they are invariably introduced during the annealing of the film.[7,18] Oxygen vacancies are donor-like, representing a positive charge at the surface.[19] Therefore, Q_T is positive in both c^+ and c^- domains. According to these considerations, the sign of the surface charge Q_S is as indicated in Table 1..

Table 1 Surface charge sign as a function of domain polarity

Polarity	Q_T	Q_P	Q_S
c^+	+	+	+
c^-	+	−	±

As PZT is a p-type material, the positive surface charge Q_S induces a hole depletion area and a downwards band bending below the surface of positive domains, as shown in Figure 2. This situation has been described in the literature as an inversion region in which PZT presents n-type behaviour[20]. Electron-hole pairs generated through illumination in the depletion region of the ferroelectric are separated by the electric field; holes are driven towards the bulk, and electrons travel to the surface, where they can take part in electrochemical reactions due to the absence of a potential barrier. This effect has been reported in the literature[6,7].

According to Table 1, in negative domains the sign of the surface charge depends on the balance between the surface state charges and the polarization charges. The two possibilities are illustrated in Figure 3. Figure 3 (a), in which $|Q_P|<Q_T$ and $Q_S>0$ is equivalent to that described for positive domains. However, as reported in a previous work[6], strong illumination at energies in excess of the bad-gap energy is required in order to obtain silver deposition in c^- domains. This suggests that the situation depicted in Figure 3 (a) is unlikely and that shown in Figure 3 (b) is the more likely situation.

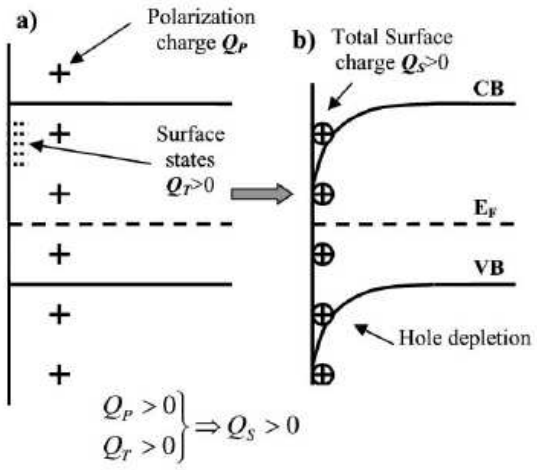

Fig. 2 In a positive domain, both the polarization charges and those due to surface states are positive. The total surface charge is therefore positive (a), which then induces a hole depletion area under the surface (b).

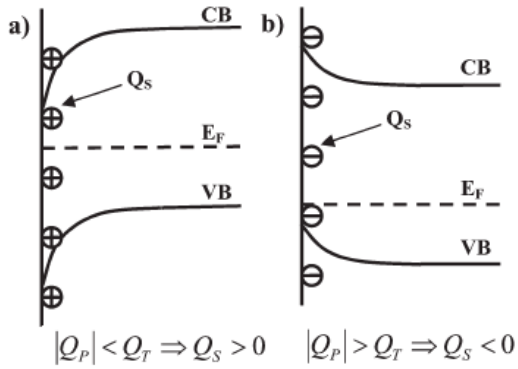

Fig. 3 The total surface charge Q_S in a negative domain depends on the relative magnitude of the polarization charge Q_P and the charge due to the surface states Q_T. The case $Q_S > 0$ is similar to the one described for positive domains (a), but it is incompatible with the experimental results. Alternatively, the case $Q_S < 0$, meaning that not all the polarization charges are compensated, is compatible with the results (b).

In the case of Figure 3 (b), the negative polarization charge is not fully compensated by the surface states, and $Q_S<0$. At the outside, a layer of positively charged adsorbates adhere to the surface. At the inside, the negative surface charge induces a hole accumulation region below the surface, and the bands are bent upwards. Under these conditions, there is a barrier for electrons at the surface of the ferroelectric that blocks the silver photo-reduction reaction. Under intense over band-gap illumination it is possible to reduce the width of hole accumulation layer enough as to enable electron tunnelling and silver reduction in negative domains[6]. However, the experimental results presented earlier (Figure 1) show that deposition on the c^- domains only happens for the [100] orientation and at a substantially reduced rate than in c^+ domains.

The experimental evidence found for c^- domains in [100] and [111] orientations is explained here in terms of their differences in remnant polarization. Reported figures of Q_P for thin film sol-gel PZT [100] and [111] orientations[15] are typically in the order of 14 $\mu C/cm^2$ and 21 $\mu C/cm^2$. An increase in the negative surface charge Q_S translates into a small increment in the width of the space charge region. But even this small difference can have a substantial impact in the number of electrons reaching the surface as the penetrability of the barrier varies exponentially with its width (see

Figure 4). A simple calculation can illustrate this point. Ignoring the contribution of external ions, the width of the space charge region w can be approximated by:

$$w = -\frac{Q_S}{qN_A}$$

where N_A is the hole density in the bulk and q is the elementary charge. The height of the barrier can be considered the same for both [100] and [111] orientations, due to the pinning of the Fermi level at the surface.[23] The penetrability T of a barrier of height E and width w can be calculated approximately by:[21]

$$T \approx e^{-2\alpha w}$$

$$\alpha = \frac{1}{\hbar}\sqrt{2mE}$$

A change ΔQ_S in surface charge from Q_{S1} to Q_{S2} will induce a change in the width of the barrier given by:

$$\Delta w = w_2 - w_1 = -\frac{Q_{S2} - Q_{S1}}{qN_A} = -\frac{\Delta Q_S}{qN_A}$$

which implies a change in the barrier penetration given by:

$$\frac{T_1}{T_2} = \exp\left(2\alpha \cdot \Delta w\right)$$

The difference in surface charge between [100] and [111] PZT is:

$$Q_S[111]\text{-}Q_S[100]=Q_P[111]\text{-}Q_P[100]=-7\mu C/cm^2$$

Using the values $N_A=10^{20}cm^{-3}$ (ref. 22) and E=1eV (ref. 23), the changes in barrier width and penetrability are Δw=6.8Å and $T[100]=3.39\cdot10^{19}\cdot T[111]$. Therefore, in negative domains the probability of electron tunnelling, and consequently of silver photo-reduction, is around 10^{19} times smaller in a [111] orientation than in a [100]. The explanation given to this effect also suggests that, under more intense illumination, it should be possible to obtain silver reduction in the [111] c^- orientation, but so far it has not been achieved.

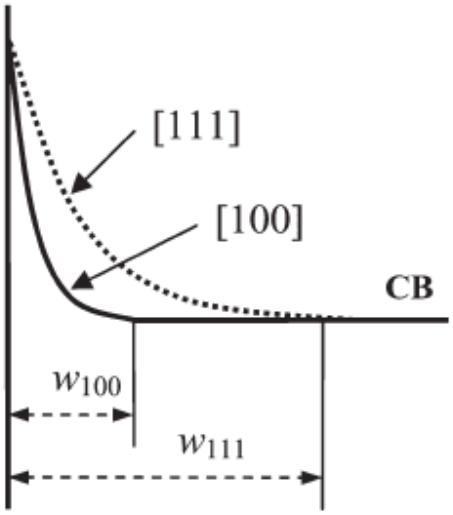

Fig. 4 The effects of a higher uncompensated polarization charge in the conduction band of a negative domain. The width of the space charge region grows with the polarization charge. Even a small change in the width of this region can have a substantial impact in the availability of electrons for photo-reduction at the surface. In a [111] material, the polarization charge is greater than in [100], explaining why silver deposits on [100] faces and not in [111].

In conclusion we have shown that variations in the remnant polarization of the ferroelectric can have a marked impact on the semi-conducting nature of the material as measured using reduction of silver nitrate to silver on the surface. The small variations in the field associated with the domain structure of the ferroelectric, in association with the low number of carriers available in the system was found to be responsible for the changes in silver metal deposition.

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